mode of reactivity, namely, halide abstraction.

Reaction of $AlCl_3$ with $(C_5H_5)_2Mo(NO)I$ in CH_2Cl_2. In view of the solvent control of the reactions of $(C_5H_5)_2Mo(NO)I$ with silver(I) salts (Figure 2), it thus appears that reaction 1 cannot be effected when Ag^+ is employed as the iodide acceptor. Mindful of our results with the AgY species, we then attempted the desired conversion with $AlCl_3$ (a harder Lewis acid than Ag^+) as the halid abstractor in CH_2Cl_2, a noncoordinating solvent. In this manner we discovered that the anticipated transformation (eq 6) does indeed occur, albeit in

$$(C_5H_5)_2Mo(NO)I + AlCl_3 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2Mo(NO)]AlCl_3I \quad (6)$$

low yield. An excess of $AlCl_3$ is required to drive the reaction to completion, and the new organometallic salt isolated is a dark red, moisture-sensitive solid, which is fairly soluble in polar organic solvents. An infrared spectrum of a dichloromethane solution of the complex exhibits a strong absorption at 1690 cm^{-1} attributable to the terminal nitrosyl ligand. This band is at a significantly higher frequency than the corresponding absorptions of the $(C_5H_5)_2Mo(NO)I$ precursor (ν_{NO} = 1642 cm^{-1}) and the $[(C_5H_5)_2Mo(NO)(CH_3CN)]^+$ cation (ν_{NO} = 1673 cm^{-1} for the SbF_6^- salt in CH_2Cl_2). Not surprisingly, the ^1H NMR spectrum of the complex in $(CD_3)_2CO$ consists of a single sharp resonance at δ 6.27 due to the equivalent η^5-C_5H_5 ligands.

The molar conductance of $[(\eta^5\text{-}C_5H_5)_2Mo(NO)]AlCl_3I$ in CH_3NO_2 is 57.5 Ω^{-1} cm^2 mol^{-1}, a value which is in the range associated with 1:1 electrolytes.[27] Interestingly, the 18-electron $[(\eta^5\text{-}C_5H_5)_2Mo(NO)]^+$ cation retains its identity in CH_3CN (i.e., ν_{NO} = 1678 cm^{-1}) and does not convert to the $[(C_5H_5)_2Mo(NO)(CH_3CN)]^+$ species (ν_{NO} = 1651 cm^{-1} in CH_3CN). Both of these observations are consistent with the complex being an ionic species rather than a Lewis acid–base adduct via a Mo—I → Al linkage. Furthermore, the second observation also indicates that $[(\eta^5\text{-}C_5H_5)_2Mo(NO)]^+$ is not an intermediate either during the formation of the acetonitrile cation by reaction 2 or during the exchange process shown in eq 3. A plausible mechanism for reaction 2 is thus

$$(C_5H_5)_2Mo(NO)I + CH_3CN \rightarrow (\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Mo(NO)(CH_3CN)I \xrightarrow{Ag^+} [(C_5H_5)_2Mo(NO)(CH_3CN)]^+$$

a sequence of steps in accord with McCleverty's proposal concerning the transitional structure of $(C_5H_5)_2Mo(NO)I$.[4] Similarly, the exchange reaction (3) must be associative.

We are currently endeavoring to optimize the yields of the $[(\eta^5\text{-}C_5H_5)_2Mo(NO)]^+$ cation and are investigating its reactivity toward a variety of nucleophiles.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this research (Grant A5885) and to The University of British Columbia for the award of a University Graduate Fellowship to C.R.N.

Registry No. $(C_5H_5)_2Mo(NO)I$, 53449-96-0; $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$, 81857-41-2; $[((\eta^5\text{-}C_5H_5)Mo(NO)(OH))_3O]BF_4$, 81898-50-2; $[((\eta^5\text{-}C_5H_5)Mo(NO)(OH))_3O]SbF_6$, 81875-62-9; $[((\eta^5\text{-}C_5H_5)Mo(NO)(OH)_3O]B(C_6H_5)_4$, 81857-43-4; $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$, 12203-25-7; $[((\eta^5\text{-}C_5H_5)Mo(NO)I)_3O]BF_4$, 81875-64-1; $[(C_5H_5)_2Mo(NO)(CH_3CN)]SbF_6$, 81875-65-2; $[(\eta^5\text{-}C_5H_5)_2Mo(NO)]AlCl_3I$, 81875-67-4; $AgBF_4$, 14104-20-2; $AgSbF_6$, 26042-64-8; $AlCl_3$, 7446-70-0.

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Catalytic Hydrogenation and Isomerization of 1-Hexene with $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$ in the Dark and under Irradiation

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The insoluble matrix of $[RhCl(CO)((CN)_2C_6H_4)]_n$ was prepared by the reaction of $[Rh(CO)_2Cl]_2$ with an equimolar amount of 1,4-diisocyanobenzene. This matrix was observed to display chemocatalytic activity under heterogeneous conditions with respect to the hydrogenation and isomerization of 1-hexene. Catalysis experiments with this matrix carried out under irradiation have led to the characterization of photoretarded catalytic 1-hexene hydrogenation and isomerization processes, photoretarded catalytic hydrogenation of 2-hexene isomers, and photoassisted catalytic initiation of hydrogenation and isomerization processes.

Introduction

Much attention has been focused in recent years on the study of the photocatalytic[1-3] and chemocatalytic[4-7] behavior of various transition-metal complexes anchored to inert support matrices. A different approach to heterogenized homogeneous catalysis may be suggested to involve insoluble coordination polymers or oligomers where the metal constitutes an integral part of the matrix. This new strategy toward catalysis is exemplified in the current study by the preparation of an insoluble matrix of the type $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$ and the investigation of its activity with respect to the hydrogenation and isomerization of 1-hexene in the dark as well as under irradiation.

Results and Discussion

Nonchelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei are of interest from the standpoint of the molecular design of some rather unusual coordination polymers. This approach has recently been demonstrated[8-10] by the preparation of numerous rho-

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dium(1+) polymers of the type $[\mathrm{Rh(diisocyanide)_2^+Cl^-}]_n$ with stereochemically rigid diisocyanide[11] linkages of different bridging geometries. Such insoluble rhodium polymers are prepared by the reaction of $[\mathrm{Rh(CO)_2Cl}]_2$ with a large molar excess of the polymerizing ligands under mild experimental conditions (eq 1). Partial substitution of the carbonyls in

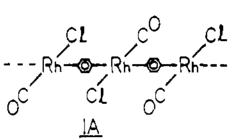
$$(n/2)[\mathrm{Rh(CO)_2Cl}]_2 + 2n(\mathrm{diisocyanide}) \rightarrow [\mathrm{Rh(diisocyanide)_2^+Cl^-}]_n + 2n\mathrm{CO} \quad (1)$$

$[\mathrm{Rh(CO)_2Cl}]_2$ with polymerizing diisocyanide ligands to afford $[\mathrm{RhCl(CO)(diisocyanide)}]_n$ may also be achieved in this system by employing equimolar quantities of the reactants (eq 2). The nature of one such system, that of $[\mathrm{RhCl(CO)}$-

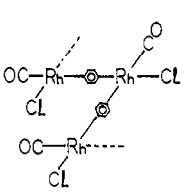
$$(n/2)[\mathrm{Rh(CO)_2Cl}]_2 + n(\mathrm{diisocyanide}) \rightarrow [\mathrm{RhCl(CO)(diisocyanide)}]_n + n\mathrm{CO} \quad (2)$$

$(1,4\text{-}(\mathrm{CN})_2\mathrm{C_6H_4})]_n$ (**1**), and some of its catalytic activities are the subject of this work.

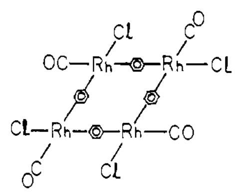
Slow addition of equimolar quantities of 1,4-diisocyanobenzene in $\mathrm{CH_2Cl_2}$ to a solution of $[\mathrm{Rh(CO)_2Cl}]_2$ in the same solvent at ambient temperature gave a dark green precipitate with the elemental composition required for **1**. Gas evolution monitored during the course of this reaction revealed the displacement of half of the carbonyl groups initially present in the starting rhodium complex. The product **1** is formed in a quantitative yield and its infrared spectrum (KBr pellet) displays bands at 2070 and 1970 $\mathrm{cm^{-1}}$, in the regions assigned to terminal isocyanide and carbonyl stretching frequencies, respectively. The diffuse-reflectance spectrum (region 350–800 nm) shows two strong absorption bands centered at 450 and 740 nm, with the latter being considerably broader. These absorptions are somewhat red-shifted compared with those reported[8] for $[\mathrm{Rh(1,4\text{-}(CN)_2C_6H_4)_2^+Cl^-}]_n$ and related coordination polymers.[9,10] The low-energy absorption in the visible-spectrum appears in a region assigned to weak intrachain Rh- - -Rh interaction in polymers[8–10] such as $[\mathrm{Rh(diisocyanide)_2^+Cl^-}]_n$ or oligomers[12,13] of the type of $[\mathrm{Rh}_n\mathrm{(CNR)}_{4n}]^{n+}$. The nonionic nature of the chlorides in **1** was inferred by the failure to effect an ion-exchange reaction in the presence of a large excess of the hexafluorophosphate anion in an ethanolic solution. Though the exact geometry of **1** is not known, the above furnished information may suggest structures resulting from either regular or irregular intrachain Rh- - -Rh interactions (3.2–3.5 Å) of units such as a linear polymer (**1A**), a nonlinear polymer (**1B**), or a tetranuclear cyclic oligomer (**1C**).



1A



1B



1C

-⊗- = 1,4-DIISOCYANOBENZENE

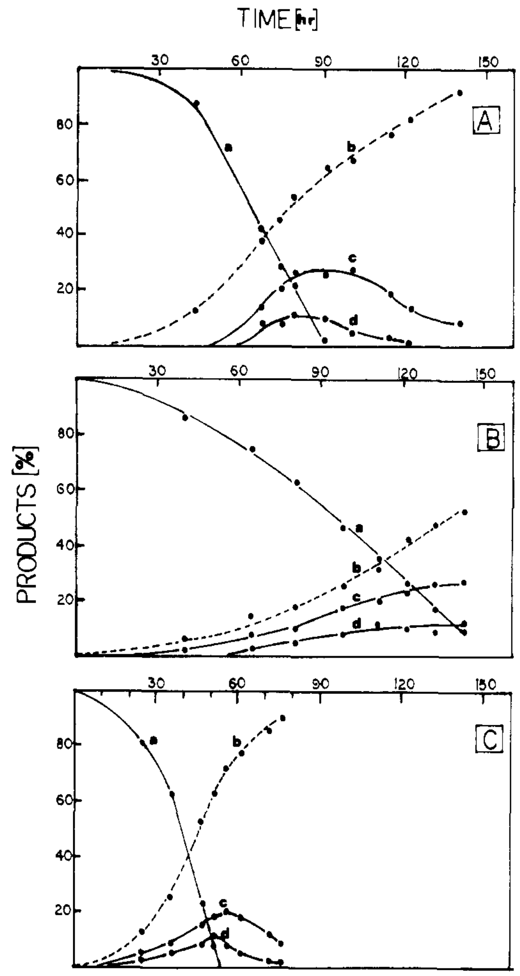


Figure 1. Catalytic hydrogenation and isomerization of 1-hexene in the presence of $[\mathrm{RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)}]_n$: chemocatalytic dark process, A; catalysis under continuous irradiation, B; photoassisted catalytic initiation (24 h) process, C. Mixture component: (a) 1-hexene; (b) *n*-hexane; (c) *trans*-2-hexene; (d) *cis*-2-hexene. The reproducibility of the experimental data is better than ±5%.

Irrespective of its exact structural geometry, the development of catalytic sites in the insoluble matrix of **1** could conceivably take place by the dissociation of the carbonyl group and breaking of the weak Rh- - -Rh interactions. The former process should be greatly facilitated under photolytic conditions (wavelength ~350 nm) as was demonstrated for example by Wrighton and co-workers[14,15] in various homogeneous metal carbonyl systems. A similar argument should also apply to the breaking of the weak Rh- - -Rh interactions in **1**, and this by analogy with the photochemical homolytic cleavage of various binuclear complexes with relatively strong metal–metal bonds (e.g.: $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{M(CO)}_n]_2$, where $n = 2$ (M = Fe,[16,17] Ru[16]), $n = 3$ [M = Mo,[18] W[19]]; $\mathrm{M_2(CO)_{10}}$ (M = Mn,[20,21] Re[22]) that have been studied extensively in recent years. These

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aspects in the context of **1** were ascertained by the attempted hydrogenation and/or isomerization of 1-hexene under photolytic conditions as well as in the dark.

The hydrogenation and isomerization experiments in the presence of **1** were carried out uniformly by using a suspension of the catalyst (0.01 g; 0.034 mmol on the basis of a monomeric unit) in 18 mL of a benzene solution of 1-hexene (0.22 M) under a constant positive hydrogen pressure of 0.5 atm at 25 °C. Progress made in these reactions was monitored periodically, and the results obtained, expressed in the form of composition (%) of products vs. time (h), are summarized in Figure 1. In the dark, hydrogenation of 1-hexene to *n*-hexane also involves isomerization to *trans*- and *cis*-2-hexenes (Figure 1A). Subsequent hydrogenation of these isomers to *n*-hexane becomes apparent at a point where most of the starting olefin has been consumed. The cis isomer is formed in smaller quantities compared with the trans isomer and disappears faster from the reaction mixture. In the presence of continuous UV irradiation, the hydrogenation reaction profile (Figure 1B) differs from that observed in the dark. Under these conditions, the consumption of 1-hexene and formation of *n*-hexane are slowed down substantially. Isomerization starts at a somewhat earlier stage in the presence of light, and this process is not followed by the hydrogenation of the isomers as was observed in the dark reaction. Irradiation only during the initial stage of the process (~24 h) has been observed to substantially accelerate the subsequent chemocatalytic dark reactions (Figure 1C). These results suggest a case of a photoassisted catalytic initiation process.

The irradiation experiment (Figure 1B) was carried out by using light with a wavelength of ~350 nm. Attempts to use higher energy light (wavelengths 253.7 and 300 nm) were observed to cause extensive damage to the insoluble matrix **1** and completely depress catalytic processes. Control experiments carried out in the absence of hydrogen, both in the dark and under irradiation, showed no sign of any isomerization processes. Another aspect, entailing the possibility of leaching of the metal from the insoluble matrix into the reaction solution, was also ascertained during this study. Several reactions in progress were stopped and filtered carefully under argon, and further hydrogenation of the filtrates was attempted. Invariably, this procedure was observed to result in the termination of both the hydrogenation and isomerization processes, thus suggesting the presence of active catalytic sites only in the insoluble matrix. The rhodium metal content of the filtrates of several complete reactions, analyzed by an atomic absorption technique, revealed essentially no leaching of metal from the insoluble matrix into the reaction solution. The infrared spectra (Nujol) of solids remaining after hydrogenation experiments show a strong band at 2150 cm^{-1}, assigned as a terminal isocyanide stretching frequency, and the absence of the original carbonyl band at 1970 cm^{-1}. This suggests that the diisocyanide linkages in **1** remain intact under the mild hydrogenation conditions employed in the course of these experiments. The dissociation of the carbonyl from **1** was observed to take place with greater facility under irradiation (~350 nm) conditions.

A more careful assessment of the hydrogenation–isomerization processes described in Figure 1 may be accomplished by considering the rates of consumption of 1-hexene and production of *n*-hexane and the olefin isomers (*trans*- and *cis*-2-hexene). The rather extended regions prior to the full consumption of 1-hexene in all of the three experiments allow one to obtain rough estimates of the maximum absolute and relative rates involved (Table I). These rates were computed by assuming that in the regions under consideration *n*-hexane is formed primarily from 1-hexene, rather than from the *trans*- and *cis*-2-hexene isomers. The absolute rates, expressed in units of mmol·h^{-1}·(mmol of Rh)$^{-1}$, furnished in Table I reveal a consistent order whereby the photoassisted catalytic initiation process [C] is the fastest, with the chemocatalytic dark process [A] being next, while the slowest process is that carried out under continuous irradiation [B]. Isomerization processes in these regions account for the formation of approximately one-third of the total products, with the rate of formation of *trans*-2-hexene being about twice that of the *cis*-2-hexene isomer. In contrast with the distinct differences between the absolute rates, the relative rates in all three processes (Table I) appear to be rather similar to each other. This observation may suggest that the effects exerted on these processes under the different experimental conditions are evenly distributed between the various components of the systems. Plausible mechanistic effects which could explain the observed absolute and relative rates in these processes will be considered next.

Table I. Some Maximum Absolute and Relative Rates Observed in the Hydrogenation and Isomerization of 1-Hexene in the Presence of $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$

process type	abs rates[a,b] [rel rates] 1-hexene	*n*-hexane	2-hexenes[c]
chemocatalytic (Figure 1A)	2.0 [3.3]	1.4 [2.3]	0.6 [1.0]
catalysis in the presence of continuous irradiation (Figure 1B)	1.1 [2.7]	0.7 [1.7]	0.4 [1.0]
photoassisted catalytic initiation (Figure 1C)	3.2 [3.2]	2.2 [2.2]	1.0 [1.0]

[a] These rates were computed from the extended nearly linear sections (1-hexene and *n*-hexane) prior to the full consumption of 1-hexene in the experiments described in Figure 1. [b] Expressed in mmol·h^{-1}·(mmol of Rh)$^{-1}$; accuracy ±5%. [c] Sums for *trans*-2-hexene and *cis*-2-hexene.

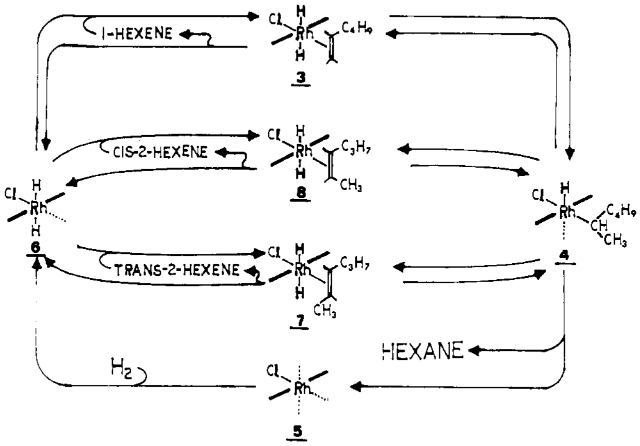

Figure 2. A proposed mechanistic view for the catalytic hydrogenation and isomerization of 1-hexene with $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$. The dotted lines stand for vacant coordination sites.

The exact mechanistic pathway of these reactions is not known and most probably may be difficult to resolve. Nevertheless, a simplified mechanistic view should be instructive in linking together the various components observed in this system (Figure 2). On the basis of an arbitrary assumption that the prevailing form of **1** is **1A**, carbonyl substitution with 1-hexene and oxidative addition of H_2 with the breaking of the weak intrachain Rh- - -Rh interactions are envisioned to give rise to an intermediate such as **3**. Rearrangement of **3** to the σ-alkyl **4**, followed by the reductive elimination of *n*-hexane, should result in **5**. The primary catalytic cycle (outer cycle) of hydrogenation could then be reestablished by the oxidative addition of H_2 to **5** and the coordination of 1-hexene

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to **6**. Olefin isomerization may be suggested to originate from **4** and link to **6** via π-olefin intermediates such as **7** (*trans*-2-hexene) and **8** (*cis*-2-hexene) (inner cycles). The reverse of the inner cycles should account for the reduction of the 2-hexenes when most of the starting olefin has been consumed. Allylic isomerization mechanisms can be ruled out since the hydrogenation and isomerization reactions do not take place in the absence of H_2. Internal olefin hydrogenation is generally more difficult than that of terminal olefins, and this feature also manifests itself in the current study. Differences in absolute rates (Table I) encountered between the chemocatalytic dark process [A] and the photoassisted catalytic initiation process [C] could be explained by the development of a smaller number of active catalytic sites under the former conditions. It is quite reasonable to anticipate that irradiation ($\sim$350 nm) will both facilitate and maximize the development of active catalytic sites in the original matrix of **1**, a point which has already been argued earlier. If the difference between processes A and B (see Figure 1) is related to the number of active sites, the relative rates should remain unaffected as indeed was observed. The slow absolute rates observed in the experiment carried out under continuous irradiation [B] may be explained by the simultaneous presence of two opposing effects. On one hand, photolysis should assist in the development of catalytic sites in the original matrix of **1** as observed in the photoassisted catalytic initiation process [C]. On the other hand, photolabilization of coordinated π-olefin intermediates such as **3**, **7**, and **8** should adversely affect the development of the catalytic cycles. The overall effects observed in this experiment [B] are those of photoretarded 1-hexene hydrogenation and isomerization processes. In the instances of the *trans*- and *cis*-2-hexene isomers, their reduction to *n*-hexane under continuous irradiation also appears to be photoretarded. If π-olefin intermediates of the types **3**, **7**, and **8**, which are concomitant to both the hydrogenation and isomerization cycles (Figure 2), are photolabilized to a similar degree under continuous irradiation, the net effect in terms of relative rates is not expected to greatly differ from those observed in the chemocatalytic dark process [A]. This contention seems to be supported by the similarity of the relative rates in all three processes (Table I).

Hydrogenation of 1-hexene in the presence of **1** was also attempted under more vigorous conditions at a constant hydrogen pressure of 20 atm and 60 °C. This experiment was carried out by using a 1-hexene to catalyst molar ratio of 1650 (0.06%) in a sealed stainless-steel autoclave. In this instance, a catalytic reaction of 20 h gave a product mixture that consisted of 93% *n*-hexane, 4% *trans*-2-hexene, and 3% *cis*-2-hexene. These results suggest an absolute rate of hydrogenation better than 77 $\text{mmol·h}^{-1}\cdot(\text{mmol of Rh})^{-1}$. This rate is substantially greater compared with those observed (Table I) under milder experimental conditions.

In the study under consideration, the precatalyst **1** is obtained as a fairly uniform polycrystalline precipitate. In catalysis experiments, carried out under constant stirring, pressure, and temperature conditions with different batches of the precatalyst, the reproducibility of the results was observed to be better than ±5%. The foregoing imply a meaningful comparison between the catalysis experiments (Figure 1). The active catalyst matrix in these experiments can be recycled without an appreciable loss in activity provided it is kept under inert atmosphere. The much faster (30–40-fold) autoclave experiment corresponds to an effective turnover number which is greater by a factor of 14 as compared with the mild-conditions experiment (Figure 1), again inferring the durability of the active catalyst **1** in this system.

Experimental Section

$[Rh(CO)_2Cl]_2$[23] and 1,4-diisocyanobenzene[11] were prepared according to published procedures. Solvents used during the course of this study were dried, deoxygenated, and freshly distilled before being used. Reactions were routinely carried out under argon atmosphere. Microanalyses were performed by the Microanalytical Laboratory of the Hebrew University of Jerusalem as well as by the Microanalytical Laboratory at the Weizmann Institute of Science.

Infrared spectra were recorded on a Perkin-Elmer 237 grating IR spectrometer and calibrated with the aid of a polystyrene film. Diffuse reflectance spectra were measured on a Cary 15 spectrometer.

Preparation of $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$ (1). A solution of 1,4-diisocyanobenzene (0.198 g, 1.55 mmol) in CH_2Cl_2 (50 mL) was added dropwise into a solution of $[Rh(CO)_2Cl]_2$ (0.3 g, 1.55 mmol) in the same solvent (50 mL) over a period of 30 min at ambient temperature. After an additional 30 min of stirring at 25 °C, the dark green precipitate of the product was filtered off, washed with CH_2Cl_2 (4 × 50 mL), and then dried under vacuum (0.1 torr (70 °C)). This procedure affords a quantitative yield of the insoluble product $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$ ($\sim$0.4 g). Anal. Calcd for $C_9H_4N_2OClRh$: C, 36.7; H, 1.36; N, 9.5; Cl, 11.9; Rh, 40.54. Found: C, 36.7; H, 1.61; N, 9.02; Cl, 11.57, Rh, 41.1. Melting point: >200 °C dec. Infrared spectrum (KBr pellet): ν(NC) 2070 (vs), ν(CO) 1970 (vs) cm^{-1}. Diffuse-reflectance spectrum (350–800 nm): strong absorptions centered at 450 and 740 (broad) nm.

Hydrogenation and Isomerization of 1-Hexene in Presence of $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$. (1) Hydrogenation at 0.5 Atm and 25 °C. Experiments were carried out uniformally with 0.01 g of **1** (0.034 mmol on the basis of a monomeric unit) suspended in 18 mL of a benzene solution of 1-hexene (0.22 M) under a constant hydrogen pressure of 0.5 atm. These experiments were performed under irradiation as well as in the dark.

The composition of the reaction mixtures during the course of these experiments was established by using a vapor-phase Hewlett-Packard Model 5750 gas chromatography instrument with a thermal conductivity detector. Separation was accomplished on a 10 ft × $^1/_8$ in. column containing 20% SE 30 on Chromosorb W at ambient temperature. Identification of products was accomplished by using coinjection procedures with the appropriate reference material.

The irradiation experiments were conducted with use of a Rayonet Photochemical Reactor, Model RPR-208, with eight RUL 3500-Å lamps yielding approximately 100 W of Black-Light ultraviolet radiation. The photolysis vessel was a thick-walled, water-jacketed Pyrex hydrogenation vessel with a sampling side arm kept at a constant temperature of 25 °C. The photolysis vessel was placed in the center of the photochemical reactor, and the stirring of the reactions was carried out magnetically with the aid of a Teflon-coated stirring bar.

Analyses for leaching of the rhodium from the insoluble matrix into the reaction solutions during the catalysis experiments were conducted with the aid of a Perkin-Elmer Model 403 atomic absorption spectrophotometer equipped with a rhodium hollow-cathode lamp (343.5 nm).

The results of the hydrogenation and isomerization catalysis experiments with 1-hexene in the presence of **1** are summarized as mixture composition (%) vs. time (h) in Figure 1. It should be instructive to point out that the 2-hexene isomers in the experiment described in Figure 1A are most probably formed in low concentrations well prior to the point of detection by gas chromatography.

(2) Hydrogenation at 20 Atm and 60 °C. A suspension of **1** (0.01 g, 0.034 mmol) in 1-hexene (7 mL, 56.1 mmol) and benzene (10 mL) was placed in a glass hydrogenation vessel inside a 100-mL stainless-steel autoclave. The autoclave was sealed and the system purged several times with hydrogen. The reaction was run at 60 °C under a constant pressure of 20 atm of H_2, supplied through a regulator system, for a period of 20 h. After completion, the reaction mixture was analyzed by the above describd GC procedure. Composition: 1-hexene, 0%; *trans*-2-hexene, 4%; *cis*-2-hexene, 3%; *n*-hexane, 93%.

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Registry No. **1**, 81740-86-5; 1-hexene, 592-41-6; $[Rh(CO)_2Cl]_2$, 14523-22-9.

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